Utilization of alkaline converted ash blends from lignite and biomass combustion for carbon capture

BOYCHEVA S.[1*], DIMITROV M.[2], ZABOV E.[1], WINTER F.[3], POPOVA M.[2]

[1]Technical University of Sofia, Department of Thermal and Nuclear Power Engineering, 8 Kl. Ohridsky Blvd., 1000 Sofia, Bulgaria

[2]Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Acad. Georgi Bonchev Str., bl. 9, 1113 Sofia

[3]TU-Wien, Institute of Chemical Technology, Environmental Technology and Life Sciences, Getreidemarkt 9, 1060 Wien

*corresponding author:
e-mail: sboycheva@tu-sofia.bg

Abstract The replacement of fossil fuels by renewable biofuels is one of the ways to limit climate change and improve the quality of the atmospheric air. For existing solid fuel combustion plants, a partial replacement of coal with biomass from wood or agriculture waste is applied. In this paper the effect of alkaline conversion of mixed coal and biomass ash to produce carbon sequestration sorbents was studied. The influence of the amount and type of biomass ash on the morphology, structure, surface characteristics and CO_2 capture capacity of the obtained products was studied.

Keywords: Biomass blended coal; Utilizations of ash mixtures; Alkaline conversion; Carbon capture

1. Introduction

Biomass is considered a renewable energy source with zero carbon emissions [1]. However, direct combustion of biomass as the main fuel, for large-scale energy production is accompanied by difficulties, the main of which is slagging in biomass combustors, which strongly hinders the heat transfer and may cause severe corrosion problems [2]. This is due to the increased content of alkaline and alkaline earth chalcogenides, carbonates and phosphates, as well as of water-soluble components in the biomass ash, which predetermines its relatively low transition and melting temperatures [3]. Biomass also has some unfavorable fuel characteristics related to increased humidity and low bulk energy density. Therefore, co-firing of biomass and pulverized coal is applied to improve environmental performance of coal combustion Thermal Power Plants (TPPs) [4]. In direct co-combustion, which is easily implemented in existing TPPs, biomass comprises 10-20 wt.% of the fuel mixture [5,6]. Biomass significantly differs from coal in its macrocomponent composition, which varies in a wide range depending on its origin [7]. Biomass contains higher share of volatile organic matter as compared to coal, and less fixed carbon and mineral part [3], while coal comprises a big variety of non-combustible minerals. The ash content is less then 1 wt.% of the

original mass for the most biomass types, while in different coal it varies in a wide range 10-20 wt.% of as-mined samples, and for some coalfields even more. This results in substantial differences in the composition of ashes from combustion of coal and biomass. Coal fly ash (CFA) contains mainly alumina, silica, aluminosilicates, iron oxides and alkaline earth oxides, and less alkaline and transition metal oxides [8]. CFA is classified in two types class F and class C depending on CaO contents regarding its utilization in building materials [9]. The categorization of biomass ash (BA) regarding its chemical composition has also been suggested, distinguishing four main types S ($SiO_2+Al_2O_3+Fe_2O_3+Na_2O+TiO_2$), C ($CaO+MgO+MnO$), K ($K_2O+P_2O_5+SO_3+Cl_2O$ and CK (between types C and K), and six sub-classes [3]. Recently, the valuable utilization of CFA by its alkaline conversion to zeolites based on its predominant aluminosilicate composition was comprehensively studied [10,11]. It has been observed that CFA zeolites are suitable adsorbents for carbon capture, remediation of polluted waters by heavy metals and organic contaminants, as well as for effective catalysts for thermal oxidation of volatile organic compounds [12-14]. Ash from direct biomass combustion is mainly used for soil amendment and fertilisation, and the production of construction materials has been studied [15]. The co-firing of coal and biomass generates a new type of ash residue, which composition and properties are not additive to the fuel mixture [16]. At the same time, it opens questions for the opportunities of ash utilization from fuel mixtures.

The current study is aimed at elucidating the effect of alkaline conversion on the characteristics and carbon capture capacity of coal and biomass ash mixtures, in comparison with the characteristics and adsorption potential of zeolitized coal ash.

2. Experimental

For the purpose of the present study, CFA from combustion of pulverized lignite with a moderate

limestone content and BA1 from mixed biomass of wood and agricultural origin were sampled from TPPs in R. Bulgaria. Biomass ash sample denoted as BA2 was collected form a local heating installation with wood pellets. Alkaline conversion was carried out with mixtures of CFA and BA with varying ratios. Sodium hydroxide was used as an alkaline activator. The reaction mixtures were subjected to an alkaline double-stage synthesis with a pre-fusion, the laboratory sequence being described elsewhere [10]. The chemical composition of raw coal and biomass ash was investigated by optical emission spectrometer with inductively coupled plasma excitation ICP 720 – OES, Agilent Technologies. The reaction mixtures were melted with the alkaline activator in nickel crucibles at 550 °C for 1 hour. The resulting cooled charges were crushed and mixed with distilled water and subjected to ultrasonic homogenization for 15 min. After conditioning, the reaction suspensions were subjected to hydrothermal activation for 4 hours. The powders were removed by filtration, washed with distilled water and dried at 105 °C and subsequently studied. The phase composition of the products were studied by X-ray diffraction (XRD) using a diffractometer Brucker D2 Phaser (Bucker Corporation, Karlsruhe, Germany) with CuKα-radiation and a Ni-filter. The morphology of the obtained products was studied by scanning electron microscopy by an apparatus Philips 515. Surface studies of the alkaline converted products were performed using an analyzer AUTOSORB iQ-MP/AG (Anton Paar GmbH, Graz, Austria) by N_2-adsorption at cryogenic temperature of −196 °C. The specific surface area and the pore size distribution were determined in the pressure range $p/p_0 = 0.002$–0.99 after preliminary degassing of the samples. The CO_2 adsorption was measured in dynamic conditions at 25 °C with 3 vol.% CO_2/N_2 at a flow rate of 30 mL/min. The samples (0.40 g) were preliminary dried at 150 °C for 1 h. The adsorption capacities were calculated based on the adsorbed amounts of CO_2 measured by gas chromatograph NEXIS GC-2030 ATF (Shimadzu, Kyoto, Japan) with a 25 m PLOT Q capillary column.

3.   Results and Discussions

Chemical composition of coal and biomass ashes used as raw materials in this study is presented in Table 1.

Table 1. Macrocomponents observed in CFA and BA

Chemical composition, wt %			
Component	CFA	BA1	BA2
SiO_2	50.80	2.31	3.84
Al_2O_3	21.33	1.01	1.42
CaO	9.36	21.01	34.83
MgO	0.82	9.27	6.50
Fe_2O_3	4.68	0.92	1.33
MnO	0.09	0.04	0.29
K_2O	2.17	6.79	9.92
Na_2O	0.37	<0.05	<0.05
P_2O_5	0.49	4.70	3.91
SO_3	0.86	1.07	3.01
TiO_2	0.78	0.03	0.08
LOI	7.80	52.82	34.72

Based on its chemical composition, CFA is classified as Class F according to ASTM C618, as $SiO_2+Al_2O_3+Fe_2O_3 > 70$ wt %. BA1 could be attributed to type CK because of the significant content of both alkaline earth oxides and K-containing phosphates, while BA2 is closer to type C because of the higher concentration of CaO+M_2O. In any case, the classification of BA1 and BA2 as class CK and C is rather conditional. According to Ref. [7], woody biomass and its ash residue commonly has a high content of alkaline earth components and refers to class C, while the agricultural biomass and its mineral combustion waste is of K type. SEM micrographs of raw ashes and their alkaline conversion products are presented in Fig. 1. CFA used is composed of indiviividual micronsized particles, many of them with spherical shape, typically for Ca-containing CFA (Fig. 1,a). BA consists of irregularly shaped agglomerates (Fig. 1,b). The alkaline conversion products were obtained at different CFA/BA ratios and constant alkalinity of the reaction solution, and are designated as follows: CB1-Z1 the (ratio CFA/BA1 is 5:2), CB1-Z2 (ratio CFA/BA1 is 5: 4), CB1-Z3 (ratio CFA/BA1 is 5:6), CFAZ (CFA is the only raw material), and CB2-Z3 (ratio CFA/BA2 is 5:6).
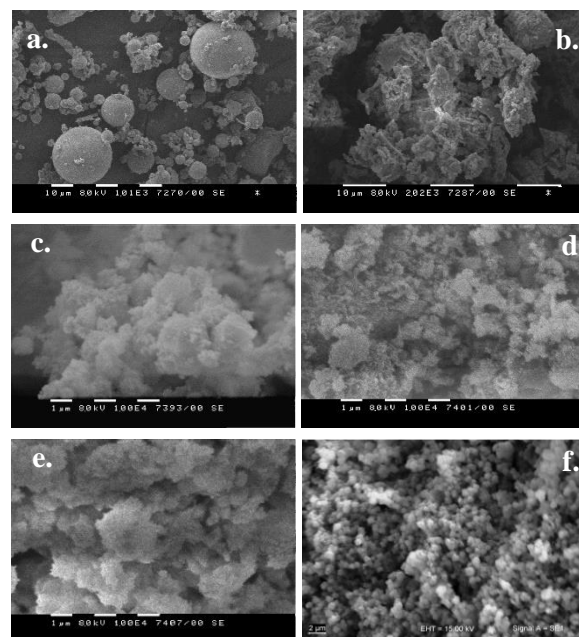

Figure 1. SEM micrographs of coal and biomass ashes and products of their alkaline conversion: a. CFA; b. BA-1; c. CB1-Z1; d. CB1-Z2; e. CB1-Z3; f. CFAZ

SEM images reveal morphology of alkaline conversion products significantly different from that of the raw materials for all investigated reaction mixtures (Fig. 1). Crystallites more distinct in the sample with less added biomass ash were observed (Fig. 1,c, sample CB1-Z1), but unlike the pure zeolitized coal ash (Fig. 1,f, sample CFAZ), no high-conversion zeolitic morphology is observed. In Fig. 2, diffractograms of samples CFAZ and CB1-Z1, and of a reference zeolite phase Na-X are presented for comparison. The product of the alkaline conversion of the studied CFA under the applied synthesis conditions is zeolite Na-X, as determined by comparison with the reference X-ray pattern of zeolite Na-X, also found in our previous studies [12]. It could be assumed that the alkaline converted products of the CFA

and BA reaction mixtures with the least added BA are also zeolite Na-X, although the main zeolite line at 2 Theta about 6 degree is not detected, but many of the other characteristic reflexes correspond to the reference XRD. This result is in accordance with the SEM analysis, as individual crystallites with hexaoctahedral shape typical of zeolite X are observed in the images (Fig.1,c). With increasing addition of BA in the reaction mixture, zeolite X was not detected. N_2-adsorption/desorption isotherms and pore size distribution functions of the alkaline conversion products are plotted in Fig. 3.
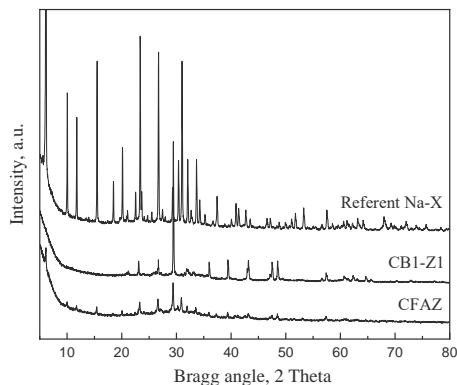

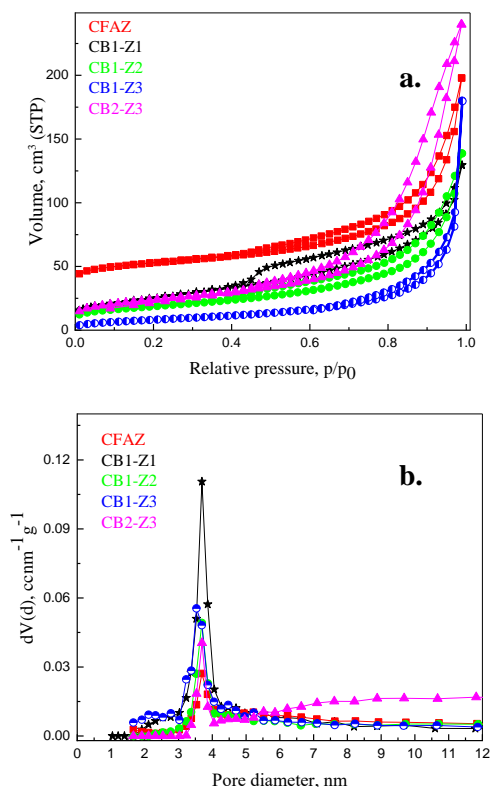**Figure 2.** XRD of coal and biomass ash alkaline converted products and a reference zeolite Na-X.

Figure 3. Surface studies of alkaline converted CFA and BA mixtures: a. N_2-adsorption/desorption isotherms; b. BJH (Barrett-Joyner-Halenda) pore size distribution curves.

Their calculated surface characteristics: specific surface area (S_{BET}), total internal volume (V_{total}) and main mesopore diameters (d) are summarized in Table 2.

It is established that the addition of BA in the reaction mixture, as well as with an increase in the ash content,

the S_{BET} of the samples decreases, which is in agreement with XRD results. This is an expected observation, considering the chemical composition of biomass ash, which includes small amounts of aluminosilicates, namely, aluminosilicate zeolitization predetermines the developed specific surface area after alkaline conversion. The main mesopore diameter does not vary with increasing BA content. At the sample CB2-Z3 synthesized with the biggest amount of woody biomass, the largest internal volume was found, probably due to the presence of large mesopores and macropores in the structure. The experimental N_2-isotherm could be assigned to type IV for the samples CFAZ and CB1-Z1, which is typical for micro-mesoporous materials. At the same time, the isotherm of CB1-Z3 could be assigned to type II which is common for nonporous or macroporous materials according to the IUPAC classification [17], while that for CB2-Z3 rather refers to type IV, indicating that the additives of different types BA into the reaction mixtures, in this case C and CK, will effect differently the characteristics of the alkaline converted products. It is also found to have a higher S_{BET} value compared to its counterpart CB1-Z3. The shape of the hysteresis loops of the isotherms is of the H3 type, which indicates wedge-shaped pores in the materials. Despite the lower values of their S_{BET}, the products of alkaline conversion of mixtures CFA and BA could exhibit a relatively good carbon sequestration capacity, due to the high content of alkaline earth and alkali oxides to participate in a chemisorption process. This provoked our interest to investigate the dynamic adsorption of CO_2 by these materials. Breakthrough curves are presented in Fig. 4, and the adsorption capacity values are summarized in Table 2.

Table 2. Surface characteristics and CO_2 adsorption capacity of alkaline converted CFA and BA mixtures

Samples	S_{BET}, m²/g	V_{total}, m³/g	d, nm	CO_2, mmol/g
CFAZ	200	0.31	3.7	3.5
CB1-Z1	90	0.20	3.7	2.4
CB1-Z2	68	0.22	3.7	2.3
CB1-Z3	31	0.28	3.5	2.2
CB2-Z3	87	0.37	3.5	1.9

A high CO_2 capture capacity of alkaline treated coal ash (sample CFAZ) is found, and with increasing the additives of BA, the value of the dynamic adsorption capacity decreases, but maintains values comparable or even better to some zeolites [18]. The comparison of the samples obtained under the same conditions from different classes BA shows a higher adsorption capacity for the CB1-Z3 prepared with BA of the CK type, and a lower one for the CB2-Z3 from C type, despite the higher specific surface value of the latter. In Fig. 4 could be observed that the adsorption zone shifts to a longer CO_2 retention time not proportional to the S_{BET} value of the samples, indicating a chemisorption or mixed physisorption and chemisorption mechanism of CO_2 capture.
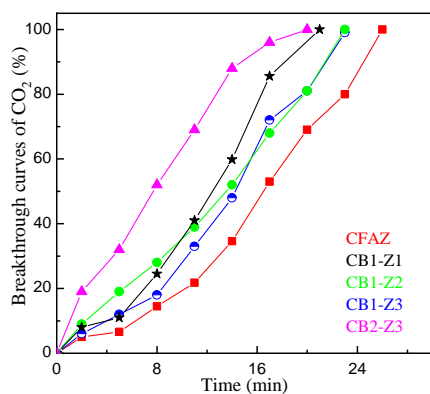
Figure 4. Breakthrough curves of CO_2 capture on coal and biomass ash alkaline converted products

4. Conclusion

Blends of coal fly ash and biomass ash of different types were processed by ultrasonic-assisted two-step alkaline conversion. It was found that increasing the additive of biomass ash disrupts the zeolitization process and lowers the surface characteristics of the products. However, the obtained materials have a relatively good CO_2 capture capacity by a predominant chemisorption mechanism. A different effect on CO_2 retention was found for products based on different types of biomass ashes.

Acknowledgements

References

[1] Saleem M. (2022), Possibility of utilizing agriculture biomass as a renewable and sustainable future energy source, *Heliyon*, 8 (2) e08905,

[2] Demirbas A. (2005), Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues, *Progress in Energy and Combustion Science*, **31** (2) 171-192.

[3] Vassilev S., Vassileva Ch., Vassilev V. (2015), Advantages and disadvantages of composition and properties of biomass in comparison with coal: An overview, *Fuel*, **158**, 330-350.

[4] Sami M., Annamalai K., Wooldridge M. (2001), Co-firing of coal and biomass fuel blends, Progress in Energy and Combustion Science, 27 (2) 171-214.

[5] https://www.etipbioenergy.eu (European Technology and Innovation Platform)

[6] Demirba A. (2003), Biomass Co-firing for Coal-Fired Boilers, *Energy exploration&exploatation*, **21** (3) 269-277.

[7] Vassilev S., Baxter D., Andersen L, Vassileva C. (2010), An overview of the chemical composition of biomass. *Fuel*, **89**, 913–933.

[8] Vassilev S., Kitano K., Takeda S., Tsurue T. (1995), Influence of mineral and chemical composition of coal ashes on their fusibility, *Fuel Processing Technology*, **45** (1) 27-51.

[9] ASTM C618 - Standard Specification for Coal Ash and Raw or Calcined Natural Pozzolan for Use in Concrete

[10] Boycheva S., Marinov I., Miteva S., Zgureva D. (2020), Conversion of coal fly ash into nanozeolite Na-X by applying ultrasound assisted hydrothermal and fusion-hydrothermal alkaline activation, *Sustainable Chemistry and Pharmacy*, **15**, art. no. 100217.

[11] Zgureva D., Boycheva S., Behunová D., Václavíková M. (2020), Smart- A nd Zero-Energy Utilization of Coal Ash from Thermal Power Plants in the Context of Circular Economy and Related to Soil Recovery, *Journal of Environmental Engineering (United States)*, **146** (8), art. no. 04020081.s

[12] Boycheva S., Zgureva D., Lazarova H., Popova M. (2021), Comparative studies of carbon capture onto coal fly ash zeolites Na-X and Na–Ca-X, *Chemosphere*, **271**, art. no. 129505.

[13] Boycheva S., Zgureva D., Miteva S., Marinov I., Behunová D.M., Trendafilova I., Popova M., Václaviková M. (2020) Studies on the potential of nonmodified and metal oxide-modified coal fly ash zeolites for adsorption of heavy metals and catalytic degradation of organics for waste water recovery, *Processes*, **8** (7), art. no. 778.

[14] Boycheva S., Szegedi Á., Lázár K., Popov C., Popova M. (2023), Advanced high-iron coal fly ash zeolites for low-carbon emission catalytic combustion of VOCs, *Catalysis Today*, **418**, art. no. 114109.

[15] Vassilev S., Baxter D., Andersen L., Vassileva Ch. (2013), An overview of the composition and application of biomass ash.: Part 2. Potential utilisation, technological and ecological advantages and challenges, *Fuel*, 105, 19-39.

[16] Kalembkiewicz J., Chmielarz U. (2012), Ashes from co-combustion of coal and biomass: New industrial wastes, *Resources, Conservation and Recycling*, **69**, 109-121.

[17] Thommes M., Kaneko K., Neimark A., Olivier J., Rodriguez-Reinoso F., Rouquerol J., Sing K.S.W. (2015) Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), *Pure Appl. Chem.* DOI 10.1515/pac-2014-1117.

[18] Indira V., Abhitha K. (2022), A review on recent developments in Zeolite A synthesis for improved carbon dioxide capture: Implications for the water-energy nexus, *Energy Nexus*, **7**, 100095.